# Search for Low Temperature Superconductivity in Graphite Compounds

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Graphite and graphite compounds with Br, K, Ca, B, ammonium, and bisulfate have been investigated for superconductivity down to 1.25°K. None became superconducting.

INVESTIGATIONS of the electrical properties of some graphite compounds have shown[1,2] that it is possible to vary the number of conduction electrons in graphite. It occurred to us that this convenient manipulation of the electron distribution might in some cases lead to superconductivity. Superconductivity is generally observed only in substances[3] in which the Fermi surface lies near the boundary of a Brillouin zone. Proximity of the Fermi surface and a zone boundary does occur in graphite and in some of its compounds. Furthermore, in common with many soft superconductors and with bismuth, graphite exhibits the de Haas-van Alphen effect.[4] Also well established is the superconductivity of certain carbides (e.g., TiC, NbC, MoC).

Accordingly, samples of graphite compounds were prepared and tested for superconductivity at low temperatures. Those samples which remained rigid during the preparation were mounted between electrical leads to measure the resistance at low temperatures. Other samples which became fragile during the reaction were sealed with helium into glass tubes and tested for appearance of the Meissner effect at low temperatures, using the method described by Hulm and Matthias.[5]

The samples were prepared from polycrystalline artificial graphite. The compounds were usually characterized by their room temperature resistance relative to unreacted graphite (Table I, column 2). Their Hall coefficients were obtained by interpolation from curves determined separately. Samples containing bisulfate were prepared by electrolysis in concentrated sulfuric acid.[1] Brominated samples were prepared in bromine atmospheres of suitable vapor pressure; their "residue compounds" were obtained by allowing bromine to escape at room temperature. Potassium and calcium compounds were prepared by the reaction of graphite with dilute solutions of the metal in liquid ammonia; the ammonium compound was obtained at a graphite cathode by electrolysis of ammonium nitrate in liquid ammonia. Washing in water converted these compounds to residue compounds. This preparation of donor compounds of graphite in liquid ammonia will be described in more detail in a separate report.

None of the samples listed in Table I showed any suggestion of superconductivity. The measurements do not exclude the possibility that superconductivity sets in at temperatures lower than those attained.

TABLE I. Samples used for superconductivity tests.

| Description of sample | Resistance relative to graphite (25°C) | Hall coefficient (emu) at 25°C | Test for superconductivity |
|---|---|---|---|
| Untreated graphite | 1 | −0.65 | Resistance down to 1.3°K |
| Bisulfate residue cmpd. | 0.44 | +0.48 | Resistance down to 1.3°K |
| Bisulfate lamellar cmpd. | 0.15 | +0.15 | Resistance down to 1.3°K |
| Potassium res. cmpd. | 0.61 | −0.78 | Resistance down to 1.3°K |
| Bromine res. cmpd. | 0.50 | +0.50 | Resistance down to 1.3°K |
| Calcium res. cmpd. | ... | ... | Meissner effect to 1.25°K |
| Potassium res. cmpd. | 0.70 | −0.78 | Meissner effect to 1.25°K |
| Bromine res. cmpd. | 0.50 | +0.50 | Meissner effect to 1.25°K |
| Bisulfate lamellar cmpd. | 0.13 | +0.13 | Meissner effect to 1.25°K |
| Ammonium res. cmpd. | 0.64 | −0.79(?) | Meissner effect to 1.25°K |
| Bromine lamellar cmpd. (saturated) | ... | ... | Meissner effect to 1.25°K |
| Graphitized lampblack, containing 0.15% boron[a] | ... | ... | Meissner effect to 1.25°K |

[a] Obtained through the courtesy of H. S. Pattin, National Carbon Company.

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3 M. Born and K. C. Cheng, Nature 161, 968, 1017 (1948); K. C. Cheng, Nature 163, 247 (1949).
4 D. Shoenberg, Nature 164, 225 (1949).
5 J. K. Hulm and B. T. Matthias, Phys. Rev. 82, 273 (1951). We wish to thank Dr. Hulm and Dr. Matthias for allowing the graphite samples to be investigated in their apparatus.